

Grignard reagent can be prepared without distillation under reduced pressure, by separating carefully the steam-distilled iodide from water and subsequently drying its ether solution with barium oxide.

The authors are grateful to W. H. Zugschwerdt and E. A. Zoellner for experimental assistance, and to the Cyrus M. Warren Fund of the American Academy of Arts and Sciences for a grant which partially defrayed expenses.

Summary

Pure 2-iodofuran has been prepared from furoic acid and iodine. It forms the corresponding Grignard reagent with uncommon ease and in excellent yields. Both compounds should prove suitable in determining the constitution of nuclear substituted furan compounds and in making accessible hitherto unavailable furan types.

AMES, IOWA

[CONTRIBUTION FROM THE ORGANIC CHEMISTRY LABORATORY OF MCGILL UNIVERSITY]

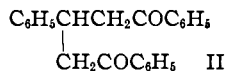
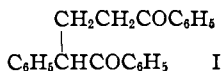
ADDITION REACTIONS OF VINYL PHENYL KETONE. II. DESOXYBENZOIN

By C. F. H. ALLEN AND W. E. BARKER¹

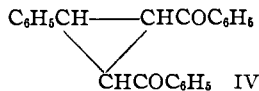
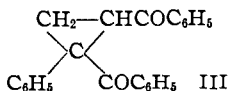
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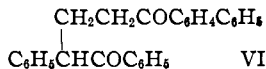
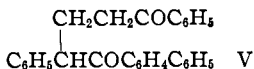
In the first paper in this series² it was shown that β -chloropropiophenone could be used in place of vinyl phenyl ketone in addition reactions. In continuation of this work we have selected desoxybenzoin as addend, and compared the reactions of the 1,5-diketone (I) thus formed with those of the isomeric benzaldiacetophenone (II).³



We have transformed it into cyclopropane derivatives (III) isomeric with those (IV) investigated by Kohler and Jones.⁴



We have also prepared two of the *p*-phenyl derivatives, one (V) by starting with *p*-phenyldesoxybenzoin and the other (VI) with *p*-phenyl- β -chloropropiophenone.



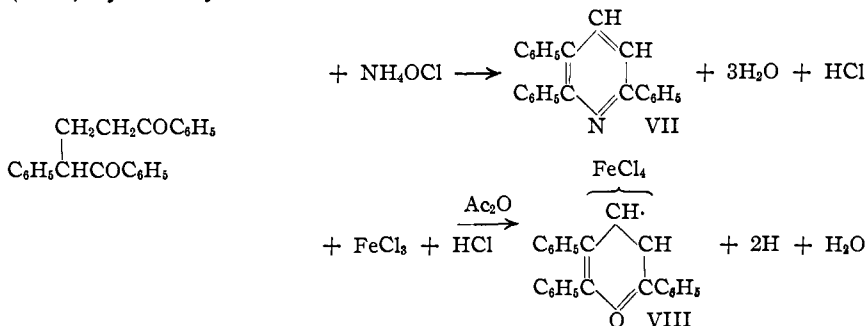
¹ Acknowledgment is hereby made of a bursary granted to one of us by the National Research Council of Canada.

² Allen and Bridgess, *THIS JOURNAL*, 51, 2151 (1929).

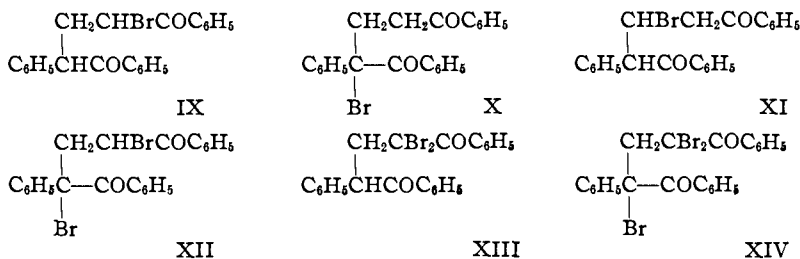
³ Kostanecki, *Ber.*, 29, 1493 (1891).

⁴ Kohler and Jones, *THIS JOURNAL*, 41, 1249 (1919).

α,β,ϵ -Triphenylpentanedione- α,ϵ (I) formed a dioxime and also gave the two characteristic reactions of a 1,5-diketone, thus proving its structure; *e. g.*, it formed a pyridine derivative (VII) when heated in alcoholic solution with hydroxylamine hydrochloride, and an oxonium ferrichloride (VIII) by Dilthey's method.⁵



Since there are two carbonyl groups, each having alpha hydrogen, a considerable number of substitution products are possible as a result of bromination (structures IX to XIV).

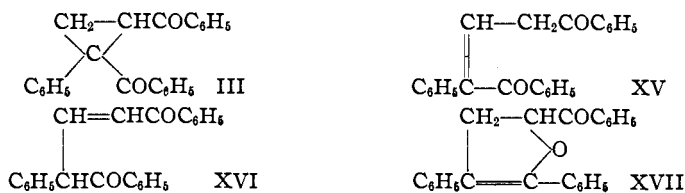


We have found two monobromides and two dibromides. Neither of the latter had any of the properties of keto-bromides, which would exclude the substances, represented by formulas XIII and XIV; accordingly they must be the stereoisomers XII.⁶ The two monobromides are the stereoisomers as depicted in IX, since one can be changed into the other by the action of hydrogen bromide. We never isolated any monobromide corresponding to formula X. It may have been a major constituent of the gummy material left after the separation of the crystalline compounds, because on further bromination this residue always gave slightly more than half the calculated amount of the dibromides.

⁵ Dilthey, *J. prakt. Chem.*, **94**, 65 (1916); **95**, 107 (1917); Dilthey and Quint, *ibid.*, **131**, 1 (1931).

⁶ Any substance having bromine in the beta position (XI) would not only be unexpected, but definitely excluded because the same bromine compounds were also produced by the action of hydrogen bromide or bromine on the cyclopropane diketones, reactions which could not by any conceivable mechanism form β -bromo compounds.

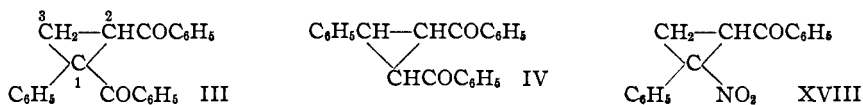
The cyclic diketones (III) were prepared by the usual methods developed by Kohler for closing a cyclopropane ring, elimination of hydrogen⁷ bromide or bromine from the various bromine substitution products. This reaction might give one of three types of substances depending on the way in which the hydrogen bromide was eliminated; (A) a cyclopropane derivative (III) if the hydrogen and bromine came from the α - γ positions. (B) An ethylenic compound (XV, XVI) if they are removed from adjoining atoms. (C) A dihydrofuran derivative (XVII) if the elimination was from an enolic modification.



Both our substances formed dioximes, therefore neither was the furan derivative. They did not reduce permanganate, form an ozonide, nor decolorize bromine instantly; they added hydrogen bromide to regenerate the original monobromide, and very slowly reacted with bromine, forming the original dibromides. This evidence, taken all together, excludes the ethylenic isomers.

We were able to obtain both the possible stereoisomeric forms of phenyl-dibenzoylcyclopropane (III), the lower melting form being much more reactive. Although they are also 1,4-diketones, we did not notice any tendency toward the formation of furan derivatives. The lower melting form was changed into its less reactive isomer by allowing it to stand in an alcoholic solution containing potassium hydroxide. Both gave the same dioxime and monophenylhydrazone. Neither was affected by concd. sulfuric acid or by phosphorus pentachloride.

The more reactive, lower melting isomer exhibited properties like those of Kohler and Jones' isomeric cyclopropane diketone (IV), with this conspicuous difference, that when the ring was broken by any reagent,



it was always opened in the 1,2-position. This is in accord with the results from the nitrocyclopropane ketone (XVIII) which was also opened only in the 1,2-position,¹ and 1,2-dibenzoylcyclopropane (XX).⁸

⁷ That the cyclopropane ring may be very easily closed in some instances is indicated by the fact that some of the cyclopropane can be isolated from the gummy residues from the preparation of the dibromide.

⁸ Conant and Lutz, *THIS JOURNAL*, **49**, 1090 (1927); the ring was opened in the 1,2-position by reduction with zinc and acetic acid, which was the only reagent reported.

Its isomer gave only intractable gums with Grignard reagents. With hydrogen bromide the lower melting cyclopropane formed the more stable monobromide (IX). With bromine the principal product was the lower melting dibromide, but there was also present a small amount of its isomer. Since the latter dibromide was also formed during the bromination, it must have the structure as represented by XII, but we were unable to regenerate the cyclopropane from it. The higher melting isomer was not affected by hydrogen bromide, and only slightly by bromine; after prolonged action of the latter reagent a small amount of the higher melting open chain dibromide (XII) was formed.

We were unable to close the cyclopropane ring from the dibromide by elimination of hydrogen bromide, and thus secure a bromocyclopropane to compare with the one of Kohler and Jones; only intractable oils resulted from all efforts in that direction.

Experimental

Preparation of Starting Materials.—Desoxybenzoin was prepared by the action of phenylacetyl chloride on benzene in the presence of anhydrous aluminum chloride; the details are described elsewhere.¹⁰

p-Phenyldesoxybenzoin was prepared by essentially the same procedure, using the same acid chloride and diphenyl¹¹ but with carbon disulfide as a solvent. After decomposing with ice and concd. hydrochloric acid the solvent and unused diphenyl were removed by steam distillation and the white product filtered and recrystallized by prolonged treatment with alcohol in a Soxhlet apparatus. The yield of ketone, melting at 151°, was 60%, based on the 68 g. of phenylacetic acid used. It has previously been prepared by Papcke.¹²

β -Chloropropiophenone was at first prepared by the directions of Hale and Britton¹³ which are satisfactory for 10–20 g. lots. With larger quantities of reacting materials, a considerable amount of benzylacetophenone was produced; this was found to occur when a small amount of acid chloride in benzene solution was in contact with a relatively large amount of anhydrous aluminum chloride. This condition exists because the violence of the reaction, as described by these authors, requires drop by drop addition of the benzene–acid chloride mixture to the dry aluminum halide. By covering the latter with a large excess of benzene, the side reaction was made insignificant. We found no α -indanone, which might be expected according to recent patents.¹⁴

The directions were modified as follows: a mixture of 50 g. of β -chloropropionic acid and 45 g. of phosphorus trichloride was heated on a boiling water-bath for an hour, 200 cc. of dry benzene added and the solution decanted onto 75 g. of anhydrous aluminum chloride covered with 200 cc. of benzene, contained in a flask under a condenser; the reaction was mild and cooling of the flask unnecessary. The mixture was refluxed for

¹⁰ "Organic Syntheses," John Wiley and Sons, Inc., New York, Vol. XII.

¹¹ We are indebted to the Dow Chemical Co., Midland, Michigan, for the diphenyl used in this work, and take this opportunity to express our appreciation of their assistance.

¹² Papcke, *Ber.*, 21, 1339 (1888).

¹³ Hale and Britton, *THIS JOURNAL*, 41, 844 (1919).

¹⁴ German Patent 485,309; Swiss Patent 126,404; *Chem. Abstracts*, 23, 613 (1929).

an hour and worked up as previously described by Hale and Britton. The yields were 62–70 g. (80 to 90%) starting with 50 g. of β -chloropropionic acid.

The necessary β -chloropropionic acid was made by both published methods.¹⁵ We found it much easier and simpler to make trimethylene chlorhydrin from the glycol and sulfur chloride;¹⁶ although it had a disagreeable odor, this disappeared during the oxidation.

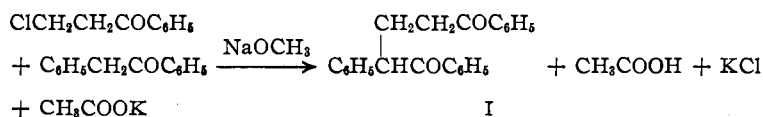
Benzylacetophenone was obtained in a 50% yield as follows: the β -chloropropionyl chloride prepared from 10 g. of the acid as previously directed was dissolved in 100 cc. of benzene and added to 30 g. of anhydrous aluminum chloride covered with 100 cc. of benzene; after refluxing one and a half hours it was decomposed by 200 g. of ice and 100 g. of concd. hydrochloric acid, the benzene extract separated, dried and solvent removed *in vacuo*. The residual brownish liquid solidified on cooling; it was washed with 25 cc. of low boiling petroleum ether and filtered; the residue weighed 8.5 g. and 1 g. more was obtained from the solution; yield, 9.5 g. (50%). It was identified by comparison with a sample on hand. This reaction is of interest because of Collet's work.¹⁷

p-Phenyl- β -chloropropiophenone, $\text{ClCH}_2\text{CH}_2\text{COC}_6\text{H}_4\text{C}_6\text{H}_5$ -4, was made by allowing 50 g. of β -chloropropionic acid to react with 35 g. of phosphorus trichloride, taking up the acid chloride with 400 cc. of carbon disulfide, and adding it, drop by drop, with vigorous stirring to a mixture of 72 g. of diphenyl, 64 g. of anhydrous aluminum chloride and 400 cc. of carbon disulfide; a precipitate soon formed in a deep green liquid. After stirring for thirty minutes, the mixture was decomposed by 2000 g. of ice and 300 g. of concd. hydrochloric acid in a 5-liter flask, and the solvent and unused diphenyl steam distilled. The contents of the flask were cooled with stirring to prevent formation of a solid cake, and the product filtered and air-dried; yield 90–94 g. (80–84%). It was purified by recrystallizing from *n*-butyl ether (1 g. required 5 cc.). The use of alcohols had to be avoided since gelatinous precipitates resulted. *p*-Phenyl- β -chloropropiophenone forms fine rosetts of needles that felt together and have a melting point of 112°. It is moderately soluble in the common organic solvents except ether and petroleum ether.

Anal. Calcd. for $\text{C}_{15}\text{H}_{13}\text{OCl}$: Cl, 14.5. Found: Cl, 14.2.

Preparation of the Diketones.—The 1,5-diketones were prepared by the reaction between the *p*-chloro ketone, desoxybenzoin, potassium acetate, and sodium methylate in methyl alcoholic solution, except with *p*-phenyldesoxybenzoin where *n*-butyl alcohol was used to secure better solubility. We were led to prepare the two phenylated diketones (V and VI) because of the difficulties encountered in handling the brominated product of the simple one; we hoped to secure less soluble derivatives with higher melting points, since it is well known that these properties are usually imparted by a phenyl group in the para position of simple substances.¹⁸ Unfortunately in this instance they were found even more difficult to manipulate so were abandoned.

α,β,ϵ -Triphenylpentanedione- α,ϵ (1) was prepared as indicated by the equation



¹⁵ "Organic Syntheses," John Wiley and Sons, Inc., New York, Vol. VIII, pp. 54, 58.

¹⁶ Derick and Bissel, *THIS JOURNAL*, **38**, 2481 (1916).

¹⁷ Collet [*Bull. soc. chim.*, [3] **17**, 66 (1897)] has studied the interaction of a number of halogenated acid chlorides and benzene, in the presence of anhydrous aluminum chloride and found that only the acyl halogen reacted.

¹⁸ Drake and Bronitsky, *THIS JOURNAL*, **52**, 3715 (1930); Morgan and Pettet, *J. Chem. Soc.*, 1125 (1931).

To 4.5 g. of β -chloropropiophenone and 8 g. of potassium acetate in 50 cc. of warm methanol¹⁹ were added 5 g. of desoxybenzoin and enough concentrated sodium methylate solution to give a definitely alkaline reaction to litmus. The reddish mixture was refluxed for an hour, acidified with acetic acid and filtered from precipitated salt, the latter being rinsed with 5 cc. of hot methanol. After three to four hours, buff colored crystals separated; these were dissolved in hot methanol (3 g. required 40 cc.), boiled with decolorizing carbon and filtered. Two recrystallizations then gave a pure white product, m. p. 95°; the average yield of a number of runs was 55%. This diketone forms large, white prisms, insoluble in petroleum ether, sparingly soluble in cold methanol, but very soluble in hot methanol and the other usual organic solvents.

Anal. Calcd. for $C_{23}H_{20}O_2$: C, 84.1; H, 6.1. Found: C, 84.0; H, 6.0.

Derivatives. (a) **Monoxime.**—The precipitated salt from a mixture of 1.4 g. of hydroxylamine hydrochloride, 4 g. of potassium acetate and 25 cc. hot alcohol was filtered and to the clear solution was added 3.3 g. of the diketone. After boiling for ten minutes and chilling the monoxime was deposited as white needles. After purification from alcohol it melted at 131°. It is insoluble in petroleum ether, sparingly soluble in ethyl ether and readily soluble in alcohol, chloroform and benzene.

Anal. Calcd. for $C_{23}H_{21}O_2N$: C, 80.4; H, 6.2. Found: C, 80.6; H, 6.0.

(b) **Dioxime.**—This was prepared in the same way, using twice the amounts of hydroxylamine hydrochloride and potassium acetate, and refluxing for three hours. It formed white needles from alcohol, m. p. 162°, with essentially the same solubilities as the monoxime.

Anal. Calcd. for $C_{23}H_{22}O_2N_2$: N, 7.8. Found: N, 8.0.

(c) **Mono-2,4-dinitrophenylhydrazone.**—This was prepared by the general method²⁰ and after crystallization from alcohol melted at 221°. It is moderately soluble in alcohol; readily soluble in ether, ethyl acetate and benzene.

Anal. Calcd. for $C_{29}H_{24}O_6N_4$: N, 10.8. Found: N, 11.0.

2,3,6-Triphenylpyridine (VII).—Two grams of the diketone and 0.9 g. of hydroxylamine hydrochloride in 25 cc. of methanol were refluxed for six hours, poured into water, and the precipitated gum crystallized from alcohol. It forms white needles, m. p. 115°, and is easily soluble in all the common solvents except petroleum ether.

Anal. Calcd. for $C_{23}H_{17}N$: C, 89.9; H, 5.5. Found: C, 89.9; H, 5.3.

This pyridine derivative gave only oils when attempts were made to form a methiodide and salt with methyl *p*-toluene sulfonate, but yielded a crystalline picrate. The latter was formed by heating to boiling 0.1 g. of the pyridine and 9.2 g. of picric acid in 5 cc. of alcohol and allowing to stand overnight. It separated from alcohol in yellow prisms, m. p. 163°; it is slightly soluble in ether and petroleum ether, readily soluble in alcohol, chloroform and benzene. For analysis, the picric acid was estimated by titration.

Anal. 0.0869 g. gave 0.0381 g. of picric acid; calcd. for $C_{29}H_{20}O_7N_4$: 0.0367 g.

α -Phenyl- γ -(*p*-phenylbenzoyl)-butyrophenone (V) was prepared by the same procedure. It forms white needles, m. p. 104°, insoluble in ether, but soluble in hot alcohol, chloroform and benzene.

Anal. Calcd. for $C_{29}H_{24}O_2$: C, 86.1; H, 5.9. Found: C, 86.0; H, 6.1.

¹⁹ Unless otherwise specified, all the methanol used in this work was the synthetic 99% material obtained from the Commercial Solvents Corporation. By "alcohol" is meant 95% ethyl alcohol.

²⁰ Allen, *THIS JOURNAL*, 52, 2955 (1930).

The dioxime was prepared as described above, and was purified, with difficulty, by dissolving in a small amount of ether and precipitating with petroleum ether. It formed a fine, white powder, m. p. 79–80°, and was readily soluble in all solvents except petroleum ether.

Anal. Calcd. for $C_{29}H_{26}O_2N_2$: N, 6.4. Found: N, 6.6.

2,3-Diphenyl-6-xenylpyridine was prepared in the same way as the triphenyl pyridine (VII). It separates from methanol, in which it is only moderately soluble, in fine, white needles, m. p. 193°; it is very soluble in benzene and chloroform.

Anal. Calcd. for $C_{29}H_{21}N$: N, 3.7. Found: N, 3.9.

γ -Phenyl- γ -(*p*-phenylbenzoyl)-butyrophenone (VI) was prepared similarly, using 5.6 g. of β -chloropropiophenone, 9.1 g. of *p*-phenyldeoxybenzoin, 10 g. of potassium acetate and 100 cc. of *n*-butyl alcohol. For purification, the butyl alcohol was removed by steam distillation, and the residual solid recrystallized from methanol; the yield was 60%. It forms white needles, m. p. 115°, that are moderately soluble in ether, petroleum ether and hot alcohol, and very soluble in benzene and chloroform.

Anal. Calcd. for $C_{29}H_{24}O_2$: C, 86.1; H, 5.9. Found: C, 85.8; H, 6.1.

The dioxime was made as previously described. It separated from methanol as a white powder, m. p. 214–215°; it is slightly soluble in hot alcohol, chloroform and benzene, but insoluble in ether and petroleum ether.

Anal. Calcd. for $C_{29}H_{26}O_2N_2$: N, 6.4. Found: N, 6.1.

The Pyryllium Salts.—These were prepared by a modification of Dilthey's method and isolated as ferrichlorides. The mechanism of the reaction is unknown but it was represented by Dilthey as shown in the introduction, although no free hydrogen ever appeared. His yields were of the order of 20%. It occurred to us that if some substance was added to remove this hydrogen as formed, the yields should be increased; we tried maleic anhydride and *p*-benzoquinone—the former was without effect, but the yields rose to 50% in the presence of one equivalent of the quinone.

One one-hundredth mole each of the diketone and quinone and 10 cc. of acetic anhydride were placed in a 100-cc. flask and 3 g. of technical ferric chloride was added; the mixture became very hot, turned dark and all the solid dissolved. When cold, the precipitated ferrichloride was filtered and washed with ether; it was analytically pure. Only intractable gums could be obtained from the filtrates, except with the *p*-phenyl substituted diketones, where small amounts were recovered unchanged. The properties are summarized in Table I.

TABLE I
SUMMARY OF PROPERTIES

No.	-Butyrophenone	M. p., °C.	Formula	Fe analysis, % Calcd. Found	
1	γ -Phenyl- γ -benzoyl- (I)	Shr. 175, m. 189	$C_{23}H_{17}OCl_4Fe$	11.0	10.8
2	γ -Phenyl- γ -(<i>p</i> -phenylbenzoyl) (VI)	Shr. 180, m. 203	$C_{29}H_{21}OCl_4Fe$	9.6	9.4
3	α -Phenyl- γ -(<i>p</i> -phenylbenzoyl) (V)	191–193	$C_{29}H_{21}OCl_4Fe$	9.6	9.6
No.	In water	H_2SO_4 addn.	Color		
1	V. s. s., slight gr. fluores.; cloudy on standing or warming	Gr. yellow partial clearing	OY		
2	Insol.	Yellow color, slightly gr.	OY		
3	Insol.	Yellow color	Brick red		

Bromination of the Diketones.—All the diketones reacted readily with bromine, but the isolation of the products proved extremely difficult, and at times we despaired of ever securing any crystalline material. In contact with solvents and hydrobromic acid the crystalline substances rapidly became oily, and after removal of the solvent only highly colored, intractable gums were left. As previously stated, two isomeric monobromides (IX) and two dibromides (XII) were obtained.

(a) **Monobromination.**—In a 500-cc. flask fitted with stirrer, reflux condenser and dropping funnel were placed 16.4 g. of the diketone (I) and 25 g. of dry chloroform; the solution was warmed to 60° and 9 g. of bromine in 25 g. of chloroform added, drop by drop, with vigorous stirring; the greenish mixture boiled vigorously as hydrogen bromide was copiously evolved. Stirring was continued for five minutes after all the bromine had been added and the solution then poured into 300 cc. of cold alcohol. The white, solid monobromide slowly separated and was filtered after four hours; the filtrate usually deposited a little more of the same solid, but on complete evaporation left only a brownish gum, which was further brominated as described below. The monobromide was purified by repeated crystallization from ethyl acetate or benzene (alcohols must be avoided). The yield of purified material was 11–13 g., 50–55%, m. p. 152°. It forms fine plates almost insoluble in alcohol, but readily soluble in hot ethyl acetate, benzene and chloroform.

The stereoisomer was not found during any preparation of the monobromide, but only by fractional crystallization of the solid resulting from dibromination. It melts at 150° (by the dip method) and a mixed melting point with the 152° form melts at 135°.

Anal. Calcd. for $C_{22}H_{19}O_2Br$: Br, 19.6. Found: (150°) Br, 19.7; (152°) Br, 19.9.

When a solution of the 150° isomer in glacial acetic acid was saturated with hydrogen bromide it was quantitatively changed into its stereoisomer.

(b) **Dibromination.**—To 32 g. of the diketone in 20 g. of dry chloroform, using the above apparatus, was added, drop by drop, 32 g. of bromine in 10 g. of the same solvent; bromination started readily after heating the flask in one spot with a match, but it was necessary to keep the temperature below 40° to get the best yields. When all the bromine had been added, 150 cc. of methanol was introduced and the flask cooled in running water for five minutes; a mixture of gum and fine needles separated and was filtered. This was dissolved in 500 cc. of boiling alcohol, filtered from 0.5 g. of insoluble residue and cooled with stirring. Final purification from methanol gave white needles, m. p. 127°. The yield was 11–13 g., or 39–40%. It is slightly soluble in ether and petroleum ether, moderately soluble in hot alcohol, but readily dissolves in benzene and chloroform.

The original filtrate, after standing overnight, deposited 7 g. (14–15%) of short thick needles of the 150° monobromide. None of this was found if the temperature of the bromination mixture rose above 40°.

On further bromination in boiling chloroform solution both monobromides yielded the 127° dibromide; a dried chloroform solution of the residual gums from monobrominations also gave small amounts of this same dibromide on further treatment with bromine.

The insoluble residue above, on fractional crystallization from ethyl acetate, was separated into 150° monobromide and a second dibromide; the latter was also formed by the action of bromine on the cyclopropane derivatives (see below). It formed diamond-shaped plates from ethyl acetate, m. p. 180°, which are sparingly soluble in hot alcohol, moderately soluble in ether and hot ethyl acetate, and very soluble in benzene and chloroform.

Anal. Calcd. for $C_{20}H_{18}O_2Br_2$: Br, 32.9. Found: (127°) Br, 32.8; (180°) Br, 32.5.

Neither dibromide could be changed into the other, but they must have structure (XII), since both are obtained by bromination of the diketone and the cyclic compounds.

The Cyclopropane Diketones (III).—Both the possible stereoisomeric cyclopropane derivatives were obtained from the two monobromides and one dibromide, and small amounts could be isolated from the residual gums from the brominations. The lower melting form was quantitatively changed into its isomer by alcoholic potash. Both forms yielded the same dioxime and monophenylhydrazone.

(a) From the Dibromide.—In a 500-cc. flask fitted with a stirrer and reflux condenser were placed 10 g. of the 127° dibromide, 10 g. of potassium iodide, 200 g. of mercury, 200 cc. of methanol, and 60 cc. of water; the whole was set on a boiling water-bath and stirred vigorously to expose as large a mercury surface as possible; the dibromide slowly dissolved and a clear yellow solution resulted after an hour. It was decanted from the mercury and filtered hot; after cooling at the tap a solid, contaminated with a little gum, separated. On recrystallization from methanol, 5 g. (75% yield) of cyclopropane was obtained. It forms white needles, m. p. 123°, which are insoluble in petroleum ether but soluble in the other solvents. The 180° dibromide was recovered unchanged after a similar treatment; the use of zinc and alcohol left an oil.

The isomeric cyclopropane diketone was prepared from this one by allowing a solution in 1% alcoholic potash to stand overnight. It forms white needles that melt at 126°, and are somewhat less soluble than the isomer in the same solvents; it is often slightly yellowish and the color is very difficult to remove.

Anal. Calcd. for $C_{23}H_{18}O_2$: C, 84.7; H, 5.5. Found: (123°) C, 84.6; H, 5.7; (126°) C, 84.9; H, 5.2.

The 126° isomer was obtained in considerable quantity by refluxing alcoholic solutions of the gummy residues accumulated during the dibrominations for five to eight hours, and allowing to stand for one to five days. Gummy, yellow crystals separated, and were dissolved in ether and filtered from traces of a yellow, insoluble substance; treated in this way, 40–45 g. of gum would yield 20–25 g. of cyclopropane. As the constituents of the gum are uncertain the mechanism of the reaction is unknown; it would certainly be remarkable that bromine or hydrogen bromide should be lost so easily from any of the possible bromo ketones.

In attempts to obtain a bromocyclopropane the dibromides were treated with one equivalent of potassium acetate; the higher melting substance was recovered unchanged, while its isomer gave an intractable gum.

(b) From the Monobromides.—The lower melting monobromide reacted with alkaline reagents to form the cyclopropane; an 8–10% alcoholic potash solution gave a 74% yield of the 126° isomer. Potassium acetate in glacial acetic acid gave a mixture of both forms, largely the higher melting isomer, in a yield of 30%. Heated for five to seven hours with potassium iodide and mercury the yield varied from 40 to 45%, but was almost entirely the lower melting form; the reaction took place without the mercury in which case it was very difficult to get a colorless product.

In marked contrast, the higher melting monobromide gave only traces of crystalline material with a great variety of alkaline reagents; from the gums thus produced, a 1–2% yield of the monophenylhydrazone of the cyclopropane diketone could be isolated, but on dissolving the gums in acetic acid and saturating with hydrogen bromide a 50–60% recovery of the same monobromide could be realized.

Dioxime.—Although both cyclopropane derivatives yielded the same dioxime when treated with hydroxylamine hydrochloride and potassium acetate in the usual manner, neither isomer was changed into the other by potassium acetate alone. A mixture of 0.5 g. of hydroxylamine hydrochloride, 1 g. of potassium acetate and 1 g. of the diketone in 20 cc. of alcohol was refluxed for twenty-four hours. It deposited

20% of the calculated amount of white needles, that were purified by recrystallizing from 50% alcohol. The dioxime melts at 212°, is moderately soluble in alcohol and readily soluble in the other solvents except petroleum ether.

Anal. Calcd. for $C_{22}H_{20}O_2N_2$: C, 77.5; H, 5.6. Found: C, 77.6; H, 5.7.

Monophenylhydrazone.—Both isomers gave the same monophenylhydrazone. Yields of the order of 2% were also obtained from the gums that resulted in all attempts to prepare the cyclopropanes from the 152° monobromide. One gram each of phenylhydrazine hydrochloride and potassium acetate was dissolved in 25 cc. of hot alcohol and filtered (pure phenylhydrazine base gave no better result), 0.5 g. of cyclic diketone added, the whole refluxed for five minutes and allowed to evaporate spontaneously. After several days, a reddish gum containing the desired substances was left; the gum was removed by washing with ether and the solid recrystallized from alcohol. The monophenylhydrazone forms fine, white needles, m. p. 169°, insoluble in ether and petroleum ether, but soluble in alcohol and chloroform.

Anal. Calcd. for $C_{20}H_{24}ON_2$: N, 6.7. Found: N, 7.0.

Reactions of the Cyclopropane Diketones.—As previously stated the only effect of alkaline reagents was to change the lower melting form into its isomer. Neither was affected by permanganate or concd. sulfuric acid, and was almost quantitatively recovered after treatment with phosphorus pentachloride in benzene solution. Neither could be reduced catalytically using Adams' catalyst. All the other reagents tried gave different results with the isomers; the lower melting form always showed the greater activity.

With zinc dust and alcohol or acetic acid, the active isomer was reduced to the open-chain diketone (I); the reaction was rapid and complete in acetic acid, but in alcohol a mixture resulted. Under the same conditions the diketone (I) was not affected.

A mixture of 0.5 g. of the 123° cyclopropane derivative, 2 g. of zinc dust, 30 cc. of alcohol and 5 cc. of water was refluxed for an hour, filtered hot, and allowed to evaporate spontaneously; it left a mixture, two-thirds rosets and the rest plates; the latter was the diketone and the former the starting material, both identified by mixed melting points. When 15 cc. of glacial acetic acid and 1 cc. of water was substituted in the above the yield of open-chain diketone was quantitative.

The less active cyclic compound was unchanged after prolonged boiling with zinc dust and alcohol, even at the boiling point of tetralin containing capryl alcohol. In acetic acid the solution quickly turned bright yellow, and a yellow solid separated; after an hour this, in suspension, was easily decanted from the heavier zinc; 0.4 g. was obtained from 0.5 g. of starting material. It is soluble in boiling xylene and aniline, very sparingly soluble in benzene, and insoluble in the other usual organic solvents, including dioxane and camphor; it melts at 282°. It did not react with bromine nor permanganate (there was a slight action on long standing), nor phenyl isocyanate, evolved methane but was recovered unchanged on treatment with methylmagnesium iodide, gave a magenta color with concd. sulfuric acid, and an oil with phosphorus pentachloride. In boiling aniline it gave values for molecular weight of the order of 3000; in the Grignard machine²¹ it showed one active hydrogen for every unit of 320–330. We did not analyze it. It was also formed in small quantities from the 152° monobromide, 127° dibromide, and gummy residues from all brominations by prolonged boiling in butyl alcoholic solution. It is, doubtless, some sort of a reduction product, possibly a condensation polymer.

The higher melting cyclopropane derivative is not affected by hydrogen bromide; its isomer reacted readily, regenerating the known monobromide, m. p. 152°—the ring was opened where it had been closed, in the 1,2-position.

²¹ Kohler and Richtmyer, *THIS JOURNAL*, **52**, 3736 (1930).

A solution of 0.5 g. of the 123° isomer in 20 cc. of glacial acetic acid was saturated with hydrogen bromide; it became warm and slightly colored. The next day a quantitative yield of the 152° dibromide had separated, and was identified by mixed melting point.

With bromine the 123° cyclopropane diketone gave mainly the 127° dibromide but there was always a small amount of its isomer, m. p. 180°. However, the higher melting cyclic compound was mainly recovered unchanged, but after prolonged treatment always gave a small amount of the 180° dibromide; the ring was again opened in the 1,2-position.

To a solution of 5 g. of the 123° cyclopropane derivative in 10 g. of chloroform was added 2.5 g. of bromine, and the mixture warmed; a trace of hydrogen bromide was noticed. After fifteen minutes, 50 cc. of methanol was added and the solution cooled in ice water for two hours; 3.2 g. of the dibromide separated—a very small amount was obtained from the filtrate, making a total yield of 43%. It was carefully fractionally crystallized into two components, mostly the 127° isomer, but always with 50–60 mg. of the 180° form. By a similar procedure, over 90% of the 126° cyclopropane was recovered unchanged; from 5 g. of starting material 20 mg. of the 180° dibromide was secured.

The two cyclopropane diketones gave different results with organic magnesium compounds. The lower melting form gave ditertiary alcohols as expected; its isomer reacted but gave only a trace of solid, the rest being a gum.

In the usual Grignard apparatus, phenylmagnesium bromide was prepared from 2 g. of magnesium, 12 g. of bromobenzene and 50 cc. of ether; the reagent was well cooled and 5 g. of the solid cyclic diketone (123°) added in small amounts. After refluxing for an hour and working up in the usual way, a 40% yield of 1-phenyl-1,2-(diphenylcarbinyl)-cyclopropane (XIX, R = C₆H₅) was obtained. It formed diamond-shaped plates, m. p. 168°, insoluble in cold alcohol, but readily soluble in hot alcohol, ether, benzene and chloroform.

Anal. Calcd. for C₃₆H₃₀O₂: C, 87.1; H, 6.2; mol. wt., 482. Found: C, 87.3; H, 5.8; mol. wt., 477.

On treatment with an excess of methylmagnesium iodide, methane was evolved, and after decomposing the complex with acid the glycol was recovered.

In the same way 1-phenyl-1,2-(phenylmethylcarbinyl)-cyclopropane was prepared from the 123° cyclopropane and methylmagnesium iodide; after acidification the product, which was insoluble in ether, was filtered; the yield was 45%. This glycol forms short, thick rods, m. p. 196°, insoluble in ether, moderately soluble in hot alcohol and hot ethyl acetate and readily soluble in benzene and chloroform.

Anal. Calcd. for C₂₅H₂₆O₂: C, 83.8; H, 7.3. Found: C, 83.6; H, 7.2.

It also was recovered unchanged when treated with an excess of methylmagnesium iodide; in the Grignard machine it consumed two moles of reagent and evolved two moles of gas.

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Summary

1. Desoxybenzoin adds to vinyl phenyl ketone to form a 1,5-diketone.
2. The diketone has been transformed into bromine substitution products, a pyridine derivative and an oxonium salt.
3. Two cyclopropane diketones were prepared from the various

bromo diketones; one is much more reactive than the other, and has been compared with a previously known structural isomer.

4. In all reactions in which the cyclopropane ring is attacked it is opened in the position in which it was closed, the 1,2-position, regardless of the nature of the reagent. This regularity is in marked contrast to the results found by previous investigators in cyclopropane chemistry.

MONTREAL, CANADA

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**SULFUR ADDITION WITH THE AID OF THIOPHOSPHORYL
CHLORIDE AND THE CATALYSIS OF TRIARYL THIOPHOSPHATE
FORMATION**

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Up to the present, thiophosphoryl chloride has not been used as a source of sulfur for the addition of sulfur to organic compounds. Some observations of this type of reaction of thiophosphoryl chloride were made and are described below.

Thiophosphoryl chloride changed triphenyl phosphite into triphenyl thiophosphate, tri-*o*-cresyl phosphite into tri-*o*-cresyl thiophosphate and diphenylmonochlorophosphite into diphenylmonochloro thiophosphate. The method of preparation consisted in mixing equimolecular amounts of organic phosphite and thiophosphoryl chloride, warming the mixture until reaction occurred, which was very violent at the start. It was completed by refluxing and the products were isolated by fractional distillation.

Phosphorus trichloride distilled over first. Then the thiophosphate formed was distilled *in vacuo*. This transfer of sulfur from the thiophosphoryl chloride to the organic phosphite proceeds without side oxidations. The thiophosphate is colorless. Sulfur additions to organic phosphites have been carried out previously by heating organic phosphites with flowers of sulfur.¹ However, in this latter method yellowish-colored side products are formed, which are not readily separated from the thiophosphate.

The addition of sulfur with the aid of thiophosphoryl chloride, as described above, affords an explanation for an interesting catalysis in thiophosphate formation. If pure thiophosphoryl chloride, rectified by distillation, is refluxed with a phenol, only little triaryl thiophosphate may be obtained. The addition of small amounts of phosphorus trichloride catalyzes the reaction in a high degree. When 3 moles of phenol are refluxed with 1 mole of very pure thiophosphoryl chloride, one obtains after seven

¹ (a) Anschütz and Emery, *Ann.*, **253**, 117, 118 (1889); (b) Walter Broeker, *J. prakt. Chem.*, [2] **118**, 287-294 (1928).